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KINETICS OF SOME METAL ATOM AND METAL FLUORIDE OXIDATION REACTIONS RELEVANT TO AIR FORCE TECHNOLOGY DEVELOPMENT.

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RESEARCH OBJECTIVES

The objectives of work under Contract F49620-77-C-0033 (J150) are to:

1. Make measurements in HTFFRs (High-Temperature Fast-Flow Reactors) of the rate coefficients and their temperature dependence (over the widest possible range from 300 K or below to $\approx$ 1900 K) of reactions between metal atoms and oxidizers such as $Al + NF_3$, $Mg + O_2$, and $B + O_2$. Selection and sequence of study are to be based on Air Force priorities.

2. Make measurements in HTFFRs of the rate coefficients and their temperature dependence for reactions between diatomic metal oxides or halides, such as those produced in reactions established in item 1, with oxidizers such as O_2, NF_3, and CO_2. Temperature range to be covered as for item 1. Selection and sequence of study to be based on Air Force priorities.

3. Provide critical analysis of the data obtained and make recommendations, where appropriate, for future action.

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I.   INTRODUCTION

Several Air Force efforts require reliable kinetic data on the formation of metal chalconides.* Specifically, (i) data on the kinetics governing the concentration of Al and B chalconides are needed to improve the delivered performance and to understand and predict plume characteristics, of rockets utilizing fluorinated solid propellants containing Al or B,[1-3] and (ii) ramjet technology requires knowledge of B and Mg oxidation by O_2.[3,4]

Until recently there were no suitable experimental techniques to provide this type of kinetic data at the required temperatures. We therefore developed the High Temperature Fast-Flow Reactor (HTFFR) specifically for measuring the kinetics of metal atom oxidation and subsequent metal chalconide radical reactions over wide temperature ranges. The HTFFR technique allows for independent control of reaction time, pressure, reactant concentrations, and temperature. It has been used for the approximate temperature range 300 to 1900 K.[5]

The methodology and potential of the HTFFR technique are discussed in depth in a book chapter[5] (prepared in this report period with partial support from this contract) which also contains a summary (with literature references) of HTFFR achievements and a review of other methods available to investigate further aspects of metal oxidation reactions. Schematics of the type of HTFFRs in current use are shown in Figs. 1-3. A metal-atom-laden stream of carrier gas (usually Ar) is produced by passing the carrier gas over a heated source of the element of interest. Rate coefficient data are obtained by measuring, at the windows, the relative metal atom and metal chalconide radical concentrations, $[Me]_{rel}$ and $[MeO]_{rel}$, as functions of the reaction condition parameters. The $[Me]_{rel}$ measurements are made in absorption and fluorescence using a hollow cathode lamp of the element of interest, while the radicals are monitored using laser-induced fluorescence. Reactions are studied under pseudo-first-order conditions with the oxidizer concentration, $[OX]$, in large excess over $[Me]$.

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* This general term includes oxides and halides.

1

70-136 H
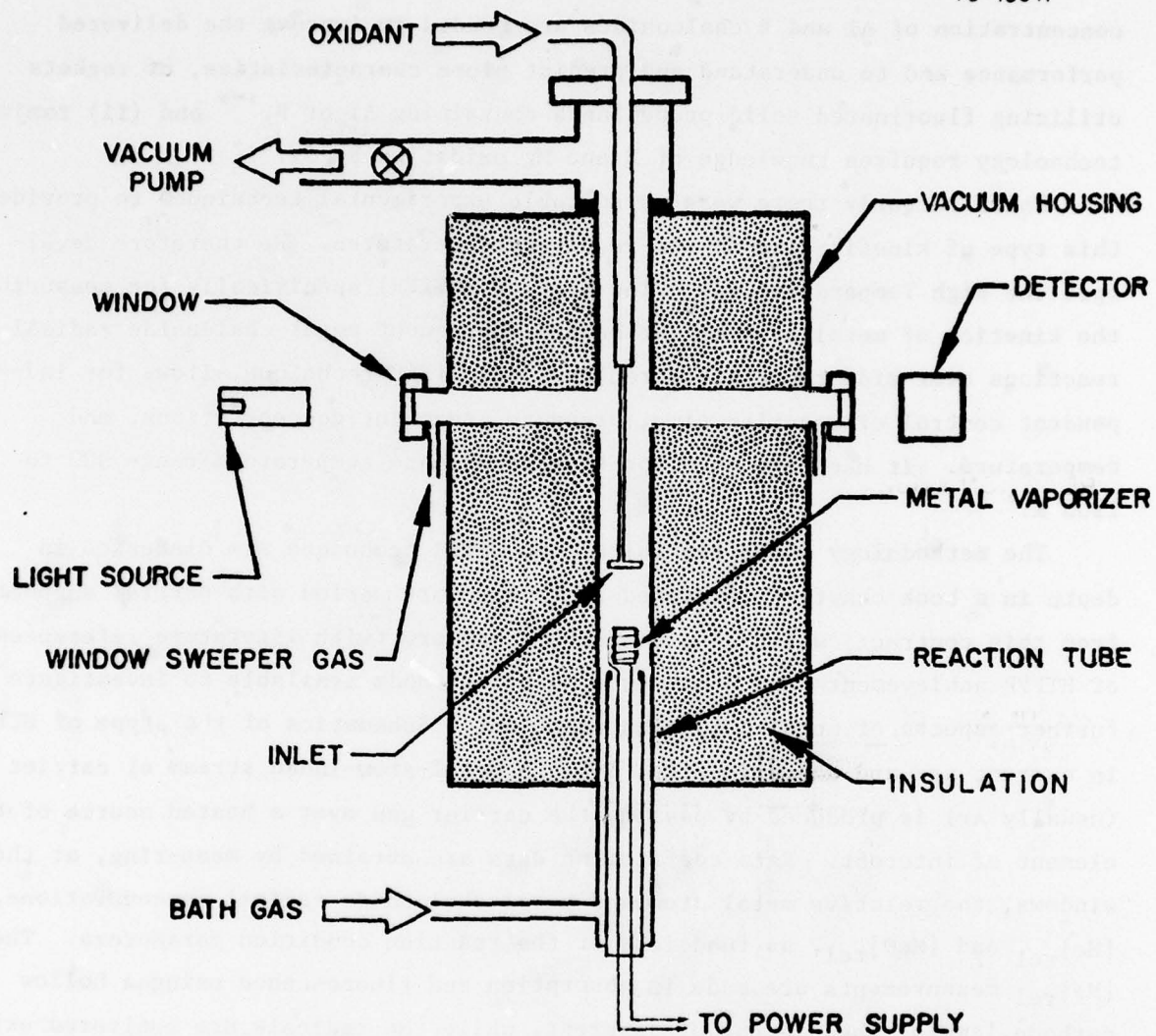
FIGURE 1   SCHEMATIC OF A SINGLE SECTION AEROCHEM HIGH-TEMPERATURE
FAST-FLOW REACTOR

2

75-83G

OXIDANT

A - THERMOCOUPLE LEADS
B - SLIDING O-RING SEAL
C - COOLANT
D - WINDOW SWEEPER GAS
E - OXIDANT INLET and THERMO-
     COUPLE WELL
F - ZIRCAR INSULATION
G - SOURCE SUPPORT TUBE
H - Pt-40% Rh RESISTANCE WIRE
J - ALUMINA HEAT SHIELD
K - BRASS VACUUM HOUSING
L - COOLING COIL
M - TO POWER SUPPLY

VACUUM PUMP ⇐

WINDOW

REACTION TUBE
(COPPER)

ALUMINA
TUBE

MAIN GAS

METAL ATOM SOURCE

SOURCE
SECTION

CARRIER GAS ⇒
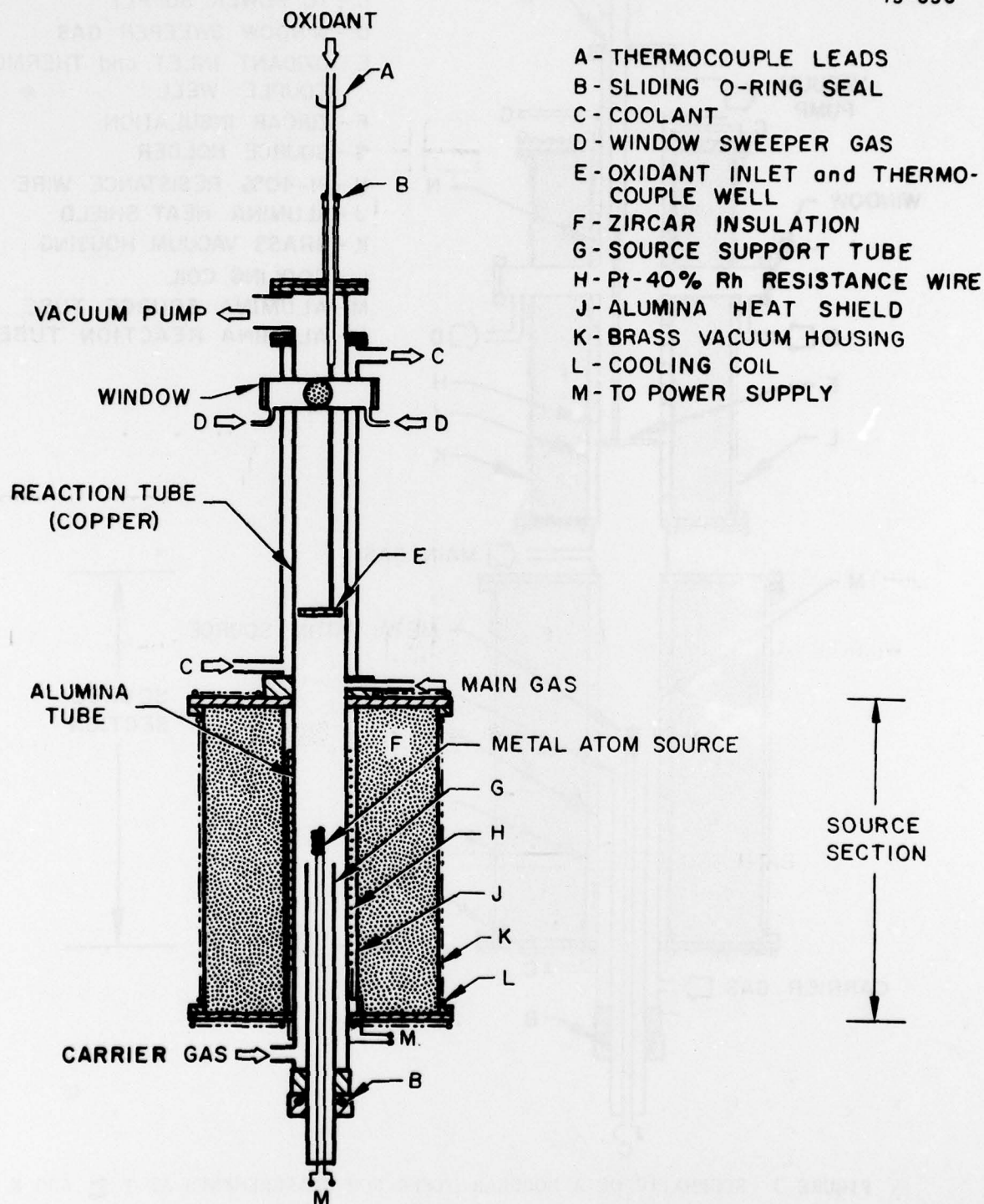
FIGURE 2   SCHEMATIC OF A MODULAR COOLED HTFFR

3

A - THERMOCOUPLE LEAD
B - SLIDING O-RING SEAL
C - TO POWER SUPPLY
D - WINDOW SWEEPER GAS
E - OXIDANT INLET and THERMO-
    COUPLE WELL
F - ZIRCAR INSULATION
G - SOURCE HOLDER
H - Pt-40% RESISTANCE WIRE
J - ALUMINA HEAT SHIELD
K - BRASS VACUUM HOUSING
L - COOLING COIL
M - ALUMINA SOURCE TUBE
N - ALUMINA REACTION TUBE

OXIDANT

VACUUM PUMP

WINDOW

MAIN GAS

METAL ATOM SOURCE

SOURCE SECTION

CARRIER GAS

FIGURE 3   SCHEMATIC OF A MODULAR HTFFR FOR MEASUREMENTS AT T $\gtrsim$ 400 K

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II. PROGRESS

A. THE Al/NF₃ REACTION

The study of the reaction

$$Al + NF_3 \rightarrow AlF + NF_2 \qquad \Delta H = -107 \pm 4 \text{ kcal mol}^{-1} \qquad (1)*$$
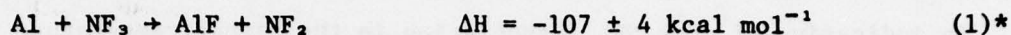
represents the first HTFFR work involving a halogen oxidizer; in all previous studies oxygen based oxidizers (O_2, N_2O, NO_2, CO_2) have been used. The NF_3 used in these experiments was made available by Kelly Air Force Base. The initial progress in the study of Reaction (1) was discussed in the first annual report on this contract,[8] which also describes the experimental methods used and the precautions taken for purification of NF_3. The reaction tube for those experiments was a 2.5 cm i.d. alumina insert tube inside a water cooled 3.1 cm i.d. Cu vacuum housing, Fig. 2. The results at that time could be summarized by the statement[8]:
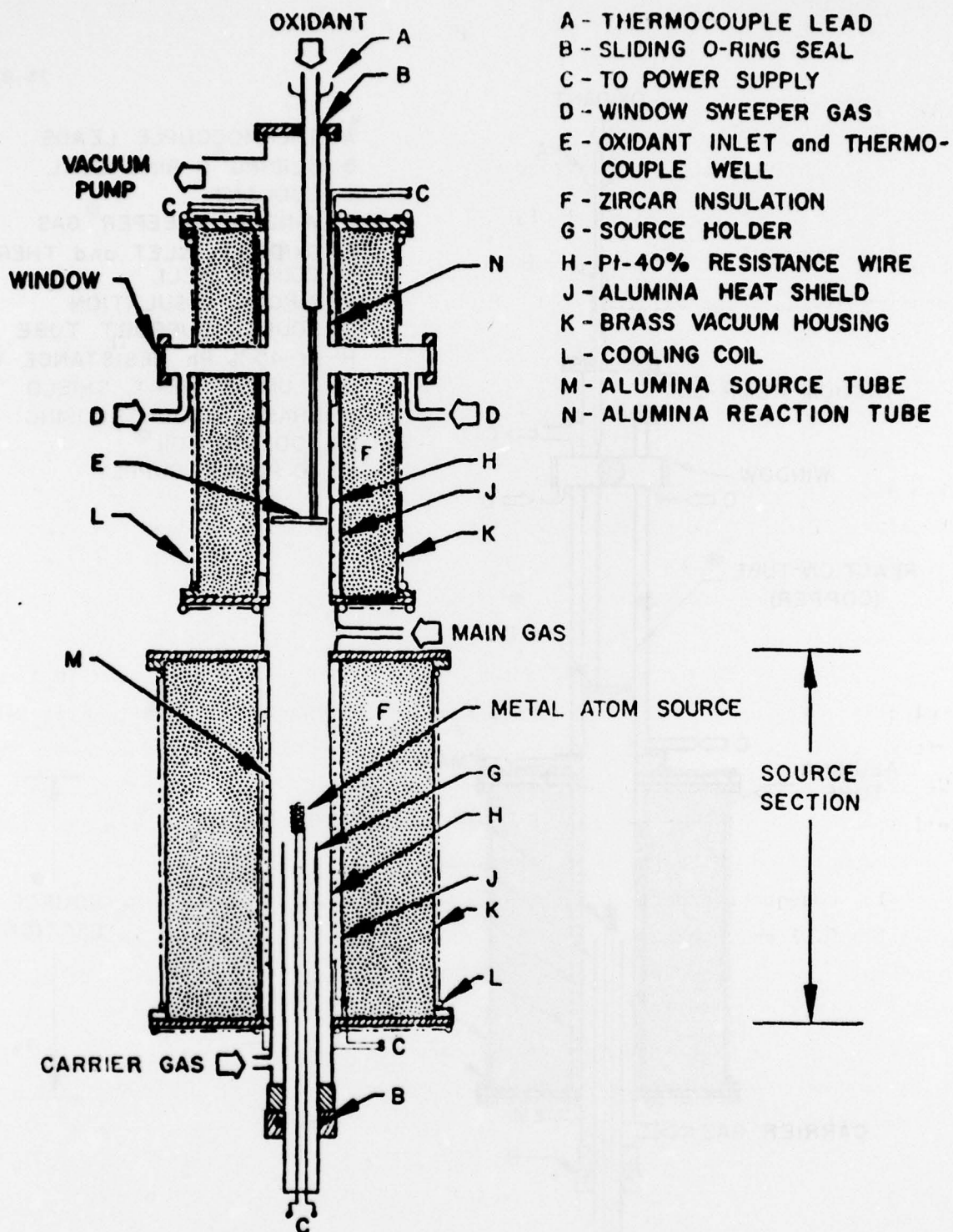
"The combined measurements now cover our usual wide range of parametric variations. Specifically we have included P = 1.3 to 17.6 Torr, $\bar{v}$ = 19 to 85 m s^{-1}, variation in $[Al]^{\text{initial}}_{\text{relative}}$ by a factor of 40, and $[NF_3]$ = 1×10^{13} to 1×10^{15} ml^{-1}. The complete set indicates a value for k_1(300 to 340 K) of (1 to 3) $\times 10^{-12}$ ml molecule^{-1} s^{-1}. However, while these results are independent of P, [Al], $[NF_3]$ and, within the limited range covered, of T, they do show a definite dependence on $\bar{v}$. We are currently assessing the possible causes of this dependence, which has to be eliminated to arrive at an accurate value for k_1. NF_3 reaction with the alumina reactor walls would be the most likely explanation."

In subsequent experiments the wall materials were therefore varied. A thin-wall ($\approx$ 0.01 cm thickness) stainless steel liner inside the 3.1 cm i.d. Cu tube gave rate coefficient data consistently higher than did the 2.5 cm i.d. alumina tube, k_1 = (2 to 5) $\times 10^{-12}$ ml molecule^{-1} s^{-1}, while a similar $\bar{v}$ dependence was obtained. A few experiments, done with an HF etched 2.5 cm i.d. Al insert tube, still showed a $\bar{v}$ dependence. A more extensive set of experiments was then performed using this Al tube coated with a material, BaF_2, which is a fully fluorinated compound and for that reason should be chemically inert to NF_3. The D(FBa-F) = 191 ± 17 kcal mol^{-1}, considerably exceeds D(Al-F) = 159 ± 2 kcal mol^{-1}; hence Al

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* ΔH values used in this document are for T = 298 K and, unless otherwise quoted, from the JANAF Tables[6] and Darwent.[7]

consumption by reaction with this fluoride material can also be excluded. The k_1 data measured when this wall coating was used was found to be $\bar{v}$ independent. Between 310 and 320 K, values of (2 to 4) $\times 10^{-12}$ were now consistently obtained, while between 325 and 340 K, k_1 was measured to be (6 to 8) $\times 10^{-12}$ ml molecule^{-1} s^{-1}. It is not clear if this difference represents a true T dependence of k_1 or is indicative of some NF_3 dissociation in the higher temperature range. To obtain an accurate $k_1(T)$ it is therefore necessary to extend the measurements over a wider temperature range. However, since equilibrium calculations[8] on the stability of NF_3 suggest that such experiments should not be extended to higher temperatures than 340 K and since small errors in the thermochemical input data could well cause even this 340 K limit to be too high, extension of the measurements to lower temperatures appears indicated.*

Lower temperatures should be achievable by using another coolant, such as liquid nitrogen. Experiments in which liquid nitrogen was forced through the cooling jacket, Fig. 2, showed, however, that too much heat exchange between the 1300-1700 K source and the reaction tube section occurred to achieve reaction zone temperatures below 300 K. We now plan to place a water-cooled flange between the source and reaction tube sections to perform T < 300 K experiments. Addition of this thermal break to the apparatus should be rather simple because of its modular construction.

B. THE B/O$_2$ REACTION

To study the reaction

$$B + O_2 \rightarrow BO + O \qquad\qquad \Delta H = -76 \pm 6 \text{ kcal mol}^{-1} \qquad\qquad (2)$$
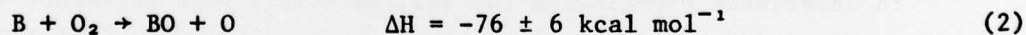
a suitable B vaporization technique must be developed. This element is considerably more refractory than any we have studied thus far in HTFFRs. From experience with other elements, a B vapor pressure of $\approx 1 \times 10^{-1}$ Torr is required in the vaporizer to achieve the [B] $\approx 1 \times 10^{-4}$ Torr in the reaction zone which is required for $k_2(T)$ measurements. This requirement translates to a vaporizer temperature of $\approx$ 2600 K,[6,10] approximately corresponding to the melting point of B.

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* It should be remembered that because of the possibility of curved Arrhenius plots,[9] extrapolation of the T $\leq$ 340 K results to much higher temperatures is not necessarily accurate.

Experiments to achieve such source temperatures in a manner compatible with HTFFR operation are in progress. From some work with our traditional resistively-heated sources[5] we concluded that these were inadequate to the task, at least in the standard HTFFR source section. The use of rf induction heating seemed potentially a more promising route. A 500 kHz, 2.5 kW Lepel induction heater Model T-2.5B was reconstituted for this purpose. Considerable effort had to be expended to match the induction coils with a susceptor and to find a crucible material suitable for containing molten B, at a cost compatible with the contract budget. These rf heating experiments were performed in Pyrex or alumina pipes (2.5 to 3.2 cm i.d.) in which the B containers and susceptors were placed and through which Ar flowed at pressures from 1-100 Torr. A coil configuration consisting of Cu tubing (0.13 cm i.d., 0.31 cm o.d.) wound tightly around the water jacket in 7 1/2 coils over a 5 cm distance was arrived at after some experimentation. The length of this tubing to the rf generator unit was 90 cm. Carbon is the most generally recommended[11] material for containing B as well as a good susceptor of rf radiation,[12-14] and hence offers the opportunity to combine the crucible and susceptor functions. Using a commercial graphite crucible we indeed readily succeeded in melting B; however, the crucible itself was attacked and developed holes within about an hour, which falls short of the time required for an HTFFR rate coefficient measurement experiment (6-8 hrs). Vitreous carbon crucibles could have been tried instead but these appear somewhat expensive for routine use. It was then decided to use a BN crucible inside a graphite susceptor (actually a BN liner inside a graphite susceptor).* Much better containment of the molten B was obtained with this arrangement, which however had the disadvantage of exposing only a small surface area to the carrier gas. Subsequent experiments using graphite rod hollowed out to provide a thick-walled crucible proved adequate for containing molten B for several hours. However, these experiments—while useful for general boron source development—revealed a further problem, i.e., the occurrence of an rf electrical discharge in the carrier gas (Ar) extending well downstream from the rf coil region. This, although rarely reported, is apparently a common occurrence in rf heating and is for most applications, quite acceptable. However, the resulting possibility of the presence of excited Ar or B atoms in

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* Direct rf heating of the BN crucible[11] was found to be insufficient for melting B, i.e., BN was inadequate as susceptor.

the reaction zone would constitute an undesirable complication in our kinetic studies. It appears somewhat improbable that this problem can be solved in a practical manner and we are therefore now pursuing some alternative approaches. These are:

(i) Direct resistive heating of B inside a thick-walled (several mm) graphite crucible, using a resistively heated thin-walled graphite, W, or Mo resistance wire. This method, similar to that used in previous HTFFR studies, would utilize a wider source section to withstand the higher temperatures and to allow the use of normal size crucibles for reasonable entrainment.

(ii) The use of a boron compound. Preliminary experiments in which 0.3% B_2H_6 in Ar was flowed through: (a) an alumina tube at 1800 K or (b) a microwave discharge (which is closely confined, unlike rf discharges) did not yield measurable B absorption. However, low B-atom yields (too low for accurate kinetic measurements) have been reported from 1% B_2H_6 in He in microwave discharge flow experiments.[15] Therefore in our next attempt at the use of a boron compound we will try 1 to 15% B_2H_6 in He mixtures decomposed by pyrolysis or microwave discharges.

Of these alternative approaches (i) is preferable since it is the cleanest method. Pyrolysis of B_2H_6 represents the next favored approach. To evaluate this method we have made equilibrium calculations in which condensed B was excluded, i.e., for the most favorable case where free B atoms have been produced, but have not yet condensed; these suggest high B yields at $\approx$ 1800 K. Of course, in complete equilibrium this B would be present as B(s) at this temperature; the potential success of this method thus depends on a much higher relative rate of B_2H_6 decomposition leading to B, than the rate of formation of this condensed phase. Whether or not this can be achieved can only be tested experimentally. These calculations do suggest that it is worth the effort to perform more pyrolysis experiments.

The microwave discharge method appears least attractive because of the larger possibility for side reactions involving other discharge-produced species. However, it is useful to remember that our extensive accurate knowledge of O- and N-atom kinetics is based, in the first place, on studies using microwave discharge production of these atoms.[16-18] Thus, though these O and N studies warn of the possibility of interfering reactions, the danger should not be exaggerated to the extent of eliminating this method from consideration.

Since the Air Force is as much interested in reactions of BF and BCl with O_2 as in the B/O_2 reaction, it would seem advisable not to devote much more time, of the limited effort allocated in the contract, on the production of free B atoms if initial results with these alternative approaches do not offer much indication of success. BF can readily be made by passing BF_3 over B at $\approx$ 2100 K and BCl by B_2Cl_4 pyrolysis at T $\approx$ 1300 K.[19] Both BF and BCl are quite volatile. $[BF]_{rel}$ and $[BCl]_{rel}$ can be measured using a flow lamp,[20] or for BCl, a frequency-doubled nitrogen pumped dye laser could be used. Studies of these monohalides would, in principle, be similar to our work on AlO,[21,22] cf. also Section II.C.2.

C. OTHER WORK

1. Measurement Accuracy

The preparation of the book chapter[5] mentioned in Section I not only allowed us to summarize our methods and techniques but also, by putting various aspects in focus, led to further theoretical investigation on the achievable accuracy of the kinetic data. The results of these investigations are included in Sections II.C-E of Ref. 5. One of these aspects, of general interest to the study of reactions at elevated temperatures, is that of the accuracy of the temperature measurement; additionally the influence of temperature on the accuracy of the measurement of free atoms in absorption is important in measurements of the kinetics of such species. A major meeting on the subject of accuracy in thermal kinetic measurements was held at the National Bureau of Standards, for which we were invited to prepare a contribution on these subjects. This required some experimental investigation the results of which are discussed in a publication[23] prepared for that meeting. The insight developed in the preparation of Refs. 6 and 23 is germane to work under the present contract. These publications should be useful as well to other Air Force efforts involving propulsion and metal oxidation.

2. O-AlO Bond Dissociation Energy

Formation of Al_2O_3 smoke from rocket exhausts is a well-recognized Air Force problem.[1-3] One potentially significant species in such smoke formation is AlO_2. There is a major controversy regarding the O-AlO bond dissociation energy, which is important to be clarified in this context. The JANAF tables[6] accept Farber's result[24] that D(O-AlO) = 120 ± 4 kcal mol^{-1}. However, several papers[25,26] have appeared that fairly convincingly demonstrate that this species

cannot have been present under Farber's operating conditions. The more generally accepted view among high temperature chemists[27] is that this bond energy cannot exceed 100 kcal mol^{-1}. However, this view contradicts our observation that the rate coefficient of the reaction AlO + O$_2$ → AlO$_2$ + O (measured by AlO disappearance, as observed by laser-induced fluorescence) has no temperature dependence, which implies[22] that D(O-AlO) $\geqq$ D(O-O) = 118 kcal mol^{-1}. Additional evidence for our observations could come from observing other AlO reactions. While the study of such reactions is not currently a major objective under the present contract, we are in the process of making some such observations, possibly as a preliminary to more extensive study in another year.

The first of these recent observations indicates, for the AlO disappearance in the AlO/CO$_2$ reaction, a rate coefficient of $\approx$ 3 × 10^{-14} ml molecule^{-1} s^{-1} at T = 750 K. A pre-exponential of 3 × 10^{-10} ml molecule^{-1} s^{-1} would appear to be an absolute upper limit for this reaction, hence exp(-E$_a$/RT) $\geqq$ 1.0 × 10^{-4} and E$_a$ $\leqq$ 13.8 kcal mol^{-1}. Since[6] D(O-CO) = 127 kcal mol^{-1}, it follows that D(O-AlO) $\geqq$ 113 kcal mol^{-1}, consistent with our earlier measurement of $\geqq$ 118 kcal mol^{-1}, but not with the 100 kcal mol^{-1} value. Experiments are in progress at other Ts which, combined with this 750 K value, should yield an activation energy directly, and thus should further refine this limit value.

III. CUMULATIVE LIST OF PUBLICATIONS

1.[*] A. Fontijn, "High-Temperature Fast-Flow Reactor Studies of Elementary Reactions," High Temperature Metal Halide Chemistry, D.L. Hildenbrand and D.D. Cubicciotti, Eds. (The Electrochemical Society, Princeton, 1978) p. 484.

2. A. Fontijn and W. Felder, "Factors Affecting the Accuracy of Rate Coefficients of Metal Atom Oxidation Reactions in Heated Flow Tubes," The Journal of Physical Chemistry 83, 24 (1979).

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[*] The publications marked with * cover several topics, not all of which are pertinent to this contract. Accordingly, they were only partially supported by this contract.

3.* A. Fontijn, "Studies of the Elementary Reaction Kinetics of High-Temperature Species Using Optical Measurement Techniques," 10th Materials Research Symposium. Characterization of High Temperature Vapors and Gases, J.W. Hastie, Ed. (National Bureau of Standards, Gaithersburg, MD, in press).

4.* A. Fontijn and W. Felder, "High Temperature Flow Tubes. Generation and Measurement of Refractory Species," Reactive Intermediates in the Gas Phase: Generation and Monitoring, D.W. Setser, Ed. (Academic Press, New York, in press).

5. A. Fontijn and W. Felder, "The O-AlO Bond Dissociation Energy," planned for publication in High Temperature Chemistry or The Journal of Chemical Physics.

IV. PROFESSIONAL PERSONNEL

In addition to Dr. Arthur Fontijn (the principal investigator), Dr. William Felder and Mr. James J. Houghton have contributed significantly to work under this contract.

V. PRESENTATIONS AND OTHER INTERACTIONS

Dr. Fontijn presented papers on the subject of measurement of the kinetics of metal atom oxidation reactions in HTFFRs at:

1. AFOSR 1977 Combustion and Plume Kinetics Meeting, AEDC, Arnold AFS, TN (April 1977).

2. Third International Symposium on Plasma Chemistry, Limoges, France (July 1977).

3. Electrochemical Society Symposium on Metal Halide Chemistry, Atlanta, GA (October 1977).

4. Physics Department, Georgia Institute of Technology, Atlanta, GA (October 1977).

5. Quantum Institute, University of California, Santa Barbara, CA (October 1977.

6. North Jersey Section, American Chemical Society, Newark, NJ (November 1977).

7. AFOSR/AFRPL 1978 Rocket Propulsion Research Meeting, Lancaster, CA (April 1978).

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8. Chemical Engineering Department, Princeton University, Princeton, NJ (May 1978).

9. The Symposium on "Current Status of Kinetics of Elementary Gas Reactions: Predictive Power of Theory and Accuracy of Measurement," NBS, Gaithersburg, MD (June 1978).

10. Gordon Conference on High Temperature Chemistry, Wolfsboro, NH (August 1978).

11. Tenth Materials Research Symposium on "Characterization of High Temperature Vapors and Gases," NBS, Gaithersburg, MD (September 1978).

12. Army Ballistics Research Laboratory, Aberdeen Proving Ground, MD (November 1978).

In addition to the planned presentation at the 1979 AFOSR/AFRPL Rocket Propulsion Research Meeting in Lancaster, CA, Dr. Fontijn has accepted invitations to talk on the subject of HTFFR kinetics studies at (i) the American Physical Society, Division of Electron and Atomic Physics Symposium on "Atoms and Molecules in Flames and Plasma" at the March 1979 Chicago meeting, and (ii) the Autumn Meeting of the Gas Kinetics Group of the (British) Chemical Society in Keele (both at no cost to this contract).

Advance copies of Ref. 5 were sent at their request to Drs. D. George and D.M. Mann of AFRPL and Dr. G.C. Light of the Aerospace Corporation for application to their work. Dr. Fontijn had several conversations with these investigators in April 1978 in Lancaster, CA, on topics of overlapping interest in metal oxidation and thermochemical aspects of rocket propulsion; with the latter two persons these conversations were continued in August 1978 during the International Combustion Symposium in Leeds, England. Several conversations on this same topic took place with Dr. M. Slack of the Grumman Corporation.

VI.   REFERENCES

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2. Air Force Systems Command Research Planning Guide, Section 5.1.2, "Rocket Exhaust Plumes," AFSC-TR-76-01, NTIS AD A029 310, May 1976.

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Oxidizers

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This experimental work is providing kinetic data on metal oxidation reactions for Air Force rocket propulsion and ramjet technology programs using the HTFFR (High-Temperature Fast-Flow Reactor) technique over the temperature range 300 to 1900 K. The reaction mechanisms and rate coefficients have been obtained from optical absorption and fluorescence measurements of the consumption of metal atoms or metal monoxide/monohalide radicals, as functions of pressure, oxidizer concentration,

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reaction time, and temperature; these variables are independently controlled.

For the study of the reaction Al + NF$_3$ → AlF + NF$_2$ it was found that to obtain data independent of average gas velocity, it was necessary to find a wall coating chemically inert to both reactants. BaF$_2$ satisfactorily fulfilled this role. Experiments using such a reaction tube coating led to a k = (2 to 4) × 10^{-12} ml molecule^{-1} s^{-1} at T about 315 K. Thermal instability of NF$_3$ prevents work at higher temperatures; thus to determine the temperature dependence of the rate coefficient, the experiments will be extended to lower temperatures.

For the study of B-atom reactions, a temperature of at least about 2600 K is required in the B-vaporization source. This was achieved by rf induction heating of boron contained inside graphite crucibles. However, the accompanying rf discharges are undesirable and alternative means for B evaporation are being tested.

Experiments on AlO reactions are consistent with our previous conclusion that the O-AlO bond energy is at least 118 kcal mol^{-1}.

Various aspects of the accuracy of kinetic measurements on metal atoms at elevated temperatures are the subject of two publications resulting from work under this contract. In one of these publications the status of HTFFR and other techniques for the study of gas-phase oxidation reactions is critically reviewed.